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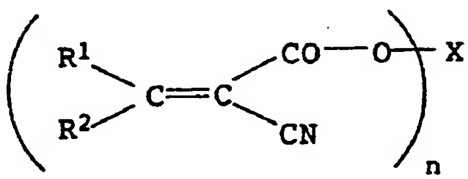
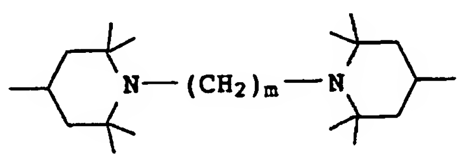
(54) **ESTERS D'ACIDE 2-CYANOACRYLIQUE**

(54) **2-CYANOACRYLIC ACID ESTERS**



I



II

(57) L'invention concerne des esters d'acide 2-cyanoacrylique (I) dans lesquels les restes ont la notation suivante: R^1 et R^2 sont hydrogène ou un reste avec une combinaison isocyclique ou hétérocyclique possédant au moins un noyau iso-aromatique ou hétéro-aromatique, l'un des restes R^1 ou R^2 devant être différent de l'hydrogène, n vaut de 2 à 10, X, lorsque n = 2, est un reste de la formule (II) où m vaut de 2 à 8, X, lorsque n > 2, est le reste d'un polyol aliphatique ou cycloaliphatique n-hydrique avec 3 à 20 atomes de C, un reste cycloaliphatique pouvant contenir également 1 à 2 hétéro-atomes, et un reste aliphatique pouvant contenir

(57) Described are 2-cyanoacrylic acid esters (I) in which the groups are defined as follows: R^1 and R^2 are hydrogen or a group with an isocyclic or heterocyclic ring system having at least one iso-aromatic or hetero-aromatic nucleus, whereby one of the groups R^1 and R^2 must be different from hydrogen, n is from 2 to 10, X in the case when n = 2 is a group of the formula (II) in which m is from 2 to 8, X in the case when n > 2 is an n-hydric aliphatic or cycloaliphatic polyol group with 3 to 20 C-atoms, whereby the cycloaliphatic polyol group may include 1 to 2 hetero-atoms and the aliphatic polyol group may include up to 8 non-adjacent oxygen atoms,

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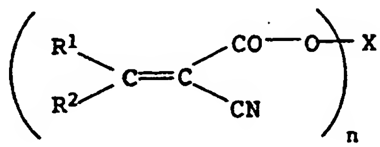
dans la chaîne carbonée jusqu'à 8 atomes d'oxygène, atomes de soufre, groupes imino ou alkylimino C_1-C_4 non adjacents. Les composés de la formule (I) s'utilisent comme filtres solaires.

sulphur atoms, imino groups or C_1-C_4 alkylimino groups in the carbon chain. Compounds of the formula (I) are suitable for use as light-protection agents.

2-Cyanoacrylic esters

Abstract

Novel 2-cyanoacrylic esters I



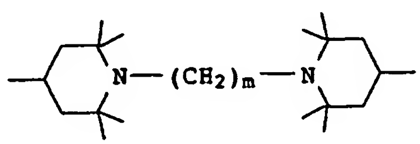
I

where the radicals have the following meanings:

R^1 and R^2 are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic nucleus, and at least one of the radicals R^1 or R^2 must be different from hydrogen,

n is from 2 to 10, and

X is, when n = 2, a radical of the formula II



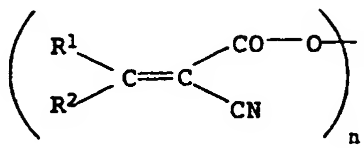
II

where m is from 2 to 8, and

X is, when n > 2, the radical of an n-hydric aliphatic or cycloaliphatic polyol having 3-20 carbon atoms, it also being possible for a cycloaliphatic radical to contain 1 or 2 hetero atoms, and for an aliphatic radical to be interrupted by up to 8 nonadjacent oxygen atoms, sulfur atoms, imino or C_1-C_4-alkylimino groups, are used as light stabilizers.

2-Cyanoacrylic esters

The present invention relates to novel 2-cyanoacrylic esters of the formula I

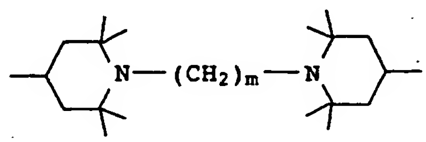


I

where R^1 and R^2 are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or heteroaromatic nucleus, and at least one of the radicals R^1 or R^2 must be different from hydrogen,

n is from 2 to 10, and

X is, when n = 2, a radical of the formula II



II

where m is from 2 to 8, and

X is, when n > 2, the radical of an n-hydric aliphatic or cycloaliphatic polyol having 3-20 carbon atoms, it also being possible for a cycloaliphatic radical to contain 1 or 2 hetero atoms, and for an aliphatic radical to be interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or C_1-C_4-alkylimino groups.

The invention furthermore relates to a process for preparing the compounds I, to the use thereof as stabilizers, in particular against the action of light, for organic materials, in particular for cosmetic or dermatological preparations, plastics or paints, and to organic materials which contain the compounds I.

US-A 3 215 725 and DE-A 41 22 475 disclose 2-cyanoacrylic esters of monohydric and dihydric alcohols as light stabilizers for plastics and paints.

However, these compounds have the technical disadvantage of a relatively high volatility. Since, moreover, they are only conditionally compatible with many organic materials, especially with polyolefins, they are prone, especially on storage at elevated temperature, to migrate and consequently display exudation.

It is an object of the present invention to remedy these disadvantages by novel stabilizers of the 2-cyanoacrylic ester type.

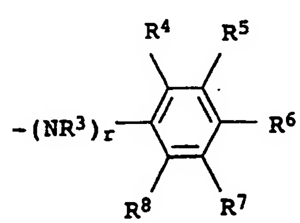
We have found that this object is achieved by the 2-cyanoacrylic esters of the general formula I defined at the outset.

We have furthermore found a process for preparing these compounds, their use as light protection factors or stabilizers for organic materials, and organic formulations which contain these compounds as stabilizers.

If the radicals R^1 and R^2 are different, the 2-cyanoacrylic ester groups of I may be either in the cis or the trans form. The preparation of the compounds usually results in mixtures of these isomers. It is possible to separate these isomers, but this is unnecessary for most industrial applications.

Suitable organic radicals for R^1 and R^2 are, in general, cyclic structures which contain at least one iso- or heteroaromatic nucleus, which is preferably linked directly to the 3-C atom of the acrylic group but can also be linked to this carbon atom via aliphatic or cycloaliphatic groups and via a linker $-NR^3-$.

R^1 or R^2 is preferably a radical of the formula III



III

where R^3 is hydrogen or C_1-C_{10}-alkyl, r is 0 or 1, and R^4 to R^8 are each, independently of one another, hydrogen, C_1-C_8-alkyl, chlorine, bromine, cyano, nitro, amino, mono(C_1-C_4-alkyl)amino, di(C_1-C_4-alkyl)amino, hydroxyl, C_1-C_8-acyl, C_1-C_8-acyloxy,

C_1-C_{18}-alkoxy, C_1-C_{12}-alkoxycarbonyl, C_3-C_6-cycloalkyl or C_3-C_6-cycloalkoxycarbonyl.

Suitable radicals R^3 besides hydrogen are C_1-C_{10}-alkyl radicals such as methyl, ethyl, n-propyl, isopropyl, isopropyl [sic], n-propyl [sic], n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, n-hexyl, n-heptyl, n-octyl, isooctyl, 2-ethylhexyl, n-nonyl, isononyl, n-decyl and isodecyl.

If one or more of the radicals R^4 to R^8 are C_1-C_8-alkyl, C_1-C_8-acyl, C_1-C_{18}-alkoxy or C_1-C_{12}-alkoxycarbonyl, the alkyl radicals therein can be, for example, methyl, ethyl, n-propyl, isopropyl, n-propyl [sic], n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, tert-pentyl, neopentyl, n-hexyl, n-heptyl, n-octyl or 2-ethylhexyl.

Examples of suitable longer-chain alkyl radicals in C_1-C_{18}-alkoxy and C_1-C_{12}-alkoxycarbonyl groups are nonyl, 2-methylnonyl, isononyl, 2-methyloctyl, decyl, isodecyl, 2-methylnonyl [sic], undecyl, isoundecyl, dodecyl, isododecyl, tridecyl, isotridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl. (The terms isooctyl, isononyl, isodecyl and isotridecyl are trivial names derived from the carbonyl compounds obtained by the oxo synthesis; compare in this connection Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A1, pages 290-293, and Vol. A10, pages 284 and 285).

Examples of suitable C_3-C_6-cycloalkyl radicals are cyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl or cyclohexyl. These cycloalkyl groups are also suitable radicals in C_3-C_6-cycloalkylcarbonyl groups.

Preferred 2-cyanoacrylic esters I are those where R^3 is hydrogen, methyl or ethyl.

Further preferred 2-cyanoacrylic esters I are those where up to three, particularly preferably one, of the radicals R^4 to R^8 are hydrogen, C_1-C_4-alkyl, chlorine, cyano, hydroxyl, acetyl, C_1-C_5-alkoxy, C_1-C_8-alkoxycarbonyl or cyclohexoxycarbonyl, and the remainder of these radicals are hydrogen.

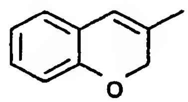
Particularly preferred 2-cyanoacrylic esters I are those where R^6 is hydroxyl, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy or tert-butoxy, because such 4-substituted phenyl groups contribute to the stabilizing effect of the compounds. For the same reason, 2-cyanoacrylic esters where R^5 and/or

R^7 are hydrogen, methyl or tert-butyl, in particular when R^6 is hydroxyl, are also particularly preferred.

Preferred compounds I according to the invention are those where r is 0.

Further preferred compounds according to the invention are those where R^1 or R^2 is hydrogen, those where R^1 and R^2 are identical radicals, and those where one of the radicals R^1 or R^2 is phenylamino, p-tolylamino, p-methoxy- or p-ethoxycarbonylphenylamino and the other is hydrogen.

Another preferred radical for R^1 or R^2 is the chroman residue Ib

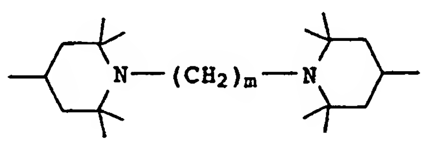


Ib

or its substituted derivates, because these also enhance the stabilizing effect of the compounds I.

Further suitable radicals R^1 and R^2 are heterocyclic groups such as substituted or unsubstituted thiophenyl [sic], furfuryl and pyridyl radicals.

If n = 2, X is a radical of the formula II

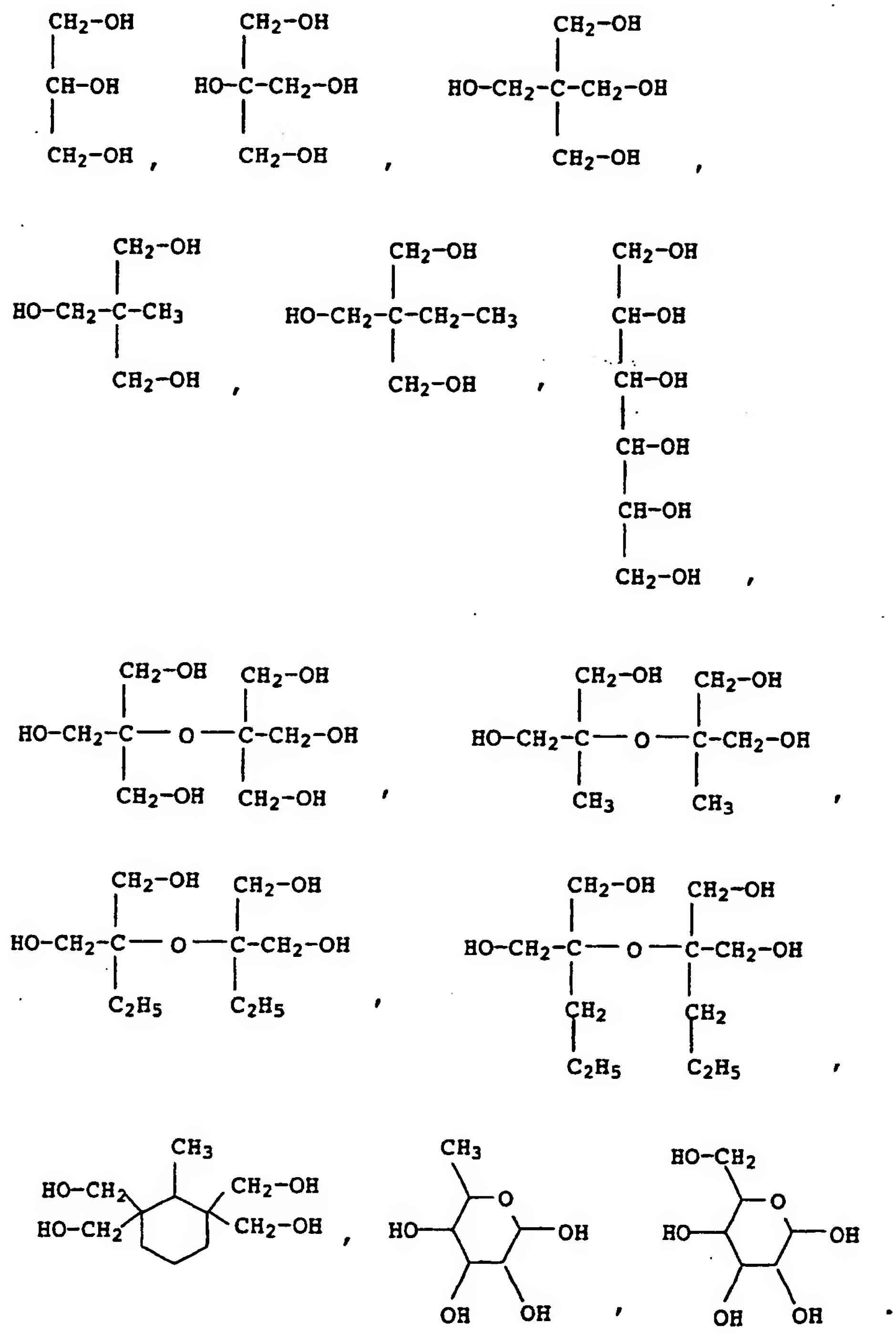


II

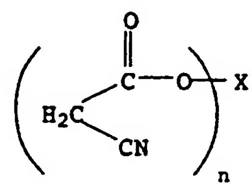
where m is from 2 to 8, preferably 2 to 6, but particularly preferably 2.

If n > 2, X is the radical of an n-hydric aliphatic or cycloaliphatic alcohol. These alcohols may be linear or branched, and their carbon chains can be interrupted by one or more oxygen or sulfur atoms, by imino groups (-NH-) or C_1-C_4-alkylimino groups.

The group X is preferably derived from the folowing known polyols:

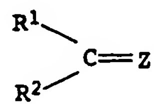


The 2-cyanoacrylic esters of the formula I where R^1 and R^2 are not linked via a nitrogen atom to the ß-C atom are preferably obtainable by reacting cyanoacetic esters of the formula III



III

with n mol of a compound (IV)

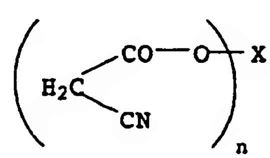


IV

under the conditions of the Knoevenagel condensation. The reaction can, for example, be carried out in aromatic solvents such as toluene or xylene (see, for example, Organikum, 1976 edition, page 572). However, polar organic solvents such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone, trialkyl orthoformate or alcohols such as n-propanol, n-butanol, ethylene glycol, diethylene glycol, ethylene glycol monomethyl ether, cyclohexanol or similar compounds are preferably used. If the starting compounds themselves form a liquid mixture, it is possible to dispense with an additional solvent. The reaction is preferably carried out at from 20 to 180°C, particularly preferably from 40 to 150°C. The pressure is preferably atmospheric pressure. The use of a catalyst or catalyst mixture may be advantageous depending on the reactivity of the compound IV employed. Examples of suitable catalysts are ammonium acetate, piperidine and ß-alanine and acetates thereof.

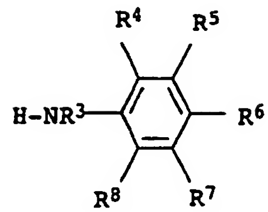
Catalysts which can additionally be used for the reaction if the reaction times are very long are Lewis acids such as $AlCl_3$, $ZrCl_4$, $TiCl_4$ or, in particular, $ZnCl_2$ in the amounts customary for this purpose.

The 2-cyanoacrylic esters of the formula I where r is 1, ie. where one radical R^1 or R^2 is linked via a nitrogen atom to the ß-C atom, can advantageously be prepared by reacting a cyanoacetic ester of the formula IV



IV

with an aromatic amine of the formula Va



Va

in the presence of trialkyl orthoformate. Examples of trialkyl orthoformates which have proven suitable are trimethyl orthoformate and triethyl orthoformate.

The cyanoacetic esters II can be prepared, for example, by reacting cyanoacetic acid or esters thereof with the appropriate polyols $X(OH)_n$ in the presence of a catalyst such as boric acid, Na_2CO_3 or K_2CO_3 or tetrabutyl orthotitanate, preferably in toluene or xylene.

The compounds according to the invention are outstandingly suitable for stabilizing organic materials against the action of light, oxygen and heat.

Examples of plastics which can be stabilized by the compounds I according to the invention are:

polymers of mono- and diolefins, eg. low and high density polyethylene, polypropylene, linear poly-1-butene, polyisoprene, polybutadiene, and copolymers of mono- or diolefins or mixtures of said polymers;

copolymers of mono- or diolefins with other vinyl monomers, eg. ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers or ethylene/acrylic acid copolymers;

polystyrene and copolymers of styrene or α-methylstyrene with dienes and/or acrylic derivatives, eg. styrene/butadiene, styrene/acrylonitrile (SAN), styrene/ethyl methacrylate, styrene/butadiene/ethyl acrylate, styrene/acrylonitrile/methacrylate, acrylonitrile/butadiene/styrene (ABS) or methyl methacrylate/butadiene/styrene (MBS);

halogenated polymers, eg. polyvinyl chloride, polyvinyl fluoride, polyvinylidene fluoride and copolymers thereof;

polymers derived from α,β unsaturated acids and derivatives thereof, such as polyacrylates, polymethacrylates, polyacrylamides and polyacrylonitriles;

polymers derived from unsaturated alcohols and amines or their acrylic derivatives or acetals, eg. polyvinyl alcohol and polyvinyl acetate;

polyurethanes, polyamides, polyureas, polyphenylene ethers, polyesters, polycarbonates, polyoxymethylenes, polysulfones, polyether sulfones and polyether ketones.

It is furthermore possible to use the compounds I according to the invention to stabilize surface coatings, eg. industrial coatings. Among these, particular attention is drawn to stoved coatings, and among these in turn to automotive coatings, preferably two-layer coatings.

The compounds I according to the invention can be added in solid or dissolved form to the coating material. Their good solubility in coating systems is a particular advantage in this context.

The compounds I according to the invention are preferably used for stabilizing polyolefins, especially polyethylene, polycarbonates, polyamides, polyesters, polystyrene, ABS and polyurethanes. It is also possible, in particular, to stabilize sheets of said plastics.

For these applications, the compounds are employed in concentrations of from 0.01 to 5% of the weight of the plastic, preferably in a concentration of from 0.02 to 2% by weight. Combination with other stabilizers, for example antioxidants, metal deactivators or other light stabilizers, and with antistatic agents or flame retardants, is often advantageous. Examples of particularly important costabilizers are sterically hindered phenols, and phosphites, phosphonites, amines and sulfur compounds.

Examples of suitable costabilizers are:

phenolic antioxidants such as
2,6-di-tert-butyl-4-methylphenol,
n-octadecyl ß-(3,5-di-tert-butyl-4-hydroxyphenol)propionate [sic],
1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane,
1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-benzene,
1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate,

1,3,5-tris[β-(3,5-di-tert-butyl-4-hydroxyphenyl) propionylethyl] isocyanurate,
1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate and pentaerythritol tetrakis[ß-(3,5-di-tert-butyl-4-hydroxy)propionate] [sic],

phosphorous-containing antioxidants such as tris(nonylphenyl) phosphite, distearyl pentaerythritol phosphite [sic],
tris(2,4-di-tert-butylphenyl) phosphite,
tris(2-tert-butyl-4-methylphenyl) phosphite,
bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite and
tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphite,

sulfur-containing antioxidants such as
dilauryl thiodipropionate,
dimyristyl thiodipropionate,
distearyl thiodipropionate,
pentaerythritol tetrakis(ß-laurylthiopropionate) and
pentaerythritol tetrakis(ß-hexylthiopropionate),

sterically hindered amines such as
bis(2,2,6,6-tetramethylpiperidyl) sebacate,
bis(1,2,2,6,6-pentamethylpiperidyl) sebacate,
bis(1,2,2,6,6-pentamethylpiperidyl) esters,
N,N'-bis(formyl)-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexanediamine,
the condensate of
1-hydroxy-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid,
the condensate of
N,N'-(2,2,6,6-tetramethylpiperidyl)hexamethylenediamine and
4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine,
poly[3-(eicosyl/tetracosyl)-1-(2,2,6,6-tetramethyl-4-piperidinyl)-2,5-pyrrolidinedione],
tris(2,2,6,6-tetramethylpiperidyl) nitrilotriacetate,
tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylic acid [sic],
1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone),
the condensates of
4-amino-2,2,6,6-tetramethylpiperidines and
tetramethylolacetylenediureas, and

2-(2'-hydroxyphenyl)benzotriazoles,
2-hydroxybenzophenones,
aryl esters of hydroxybenzoic acids,
α-cyanocinnamic acid derivatives,

nickel compounds or
oxanilides.

The compounds I according to the invention can be mixed, in particular with plastics, using all known apparatus and methods for mixing stabilizers or other additives into polymers.

The 2-cyanoacrylic esters I according to the invention are distinguished by high compatibility with conventional types of plastic and by good solubility and excellent compatibility in conventional coating systems. As a rule, they have very little or no intrinsic color, are stable and nonvolatile at conventional plastic- and surface coating-processing temperatures and afford long-lasting protection to the materials treated with them. Above all, however, they show virtually no tendency to migrate in plastics.

UV radiation is divided into three regions: the UV-A region (320-400 nm), the UV-B region (290-320 nm) and the UV-C region (200-290 nm). The high-energy UV-C region is predominantly absorbed by the ozone layer. Radiation in the UV-B region is responsible in particular for the development of sunburn and skin cancer. UV-A radiation produces on lengthy exposure tanning of the skin but is also partly responsible for aging of the skin.

Because of the favorable solubility properties and the good absorption properties, especially in the UV-A region, the compounds according to the invention are particularly suitable for applications in cosmetics and dermatological products. The compounds can also be used advantageously for protecting cosmetic products such as perfumes, creams and lotions. Combinations with sunscreen agents which absorb in the UV-B region are particularly preferred. The 2-cyanoacrylic esters I are used for cosmetic formulations in concentrations of from 0.05 to 15%, preferably from 0.1 to 10%, of the total weight of the cosmetic formulation.

Other organic materials to which the compounds according to the invention can advantageously be added are pharmaceutical formulations such as pills and suppositories, photographic recording materials, especially photographic emulsions, and precursors for plastics and paints.

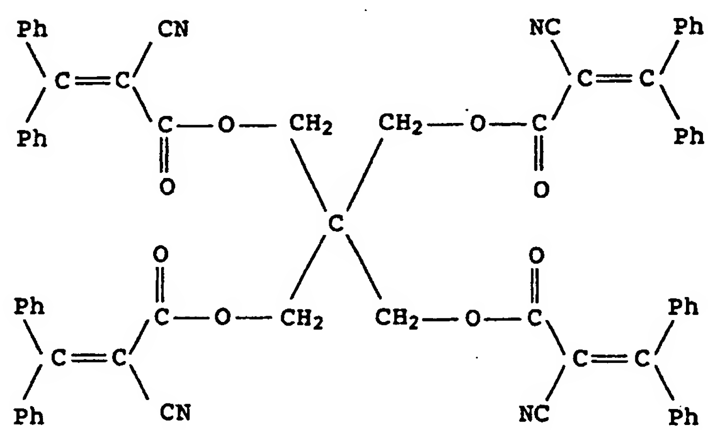
Examples

Preparation Examples

Example 1

16.2 g (0.04 mol) of 2,2-bis(hydroxymethyl)-1,3-propanediol tetracyanoacetate were dissolved in 100 ml of N,N-dimethylformamide (DMF) and heated to 80°C. To this were added dropwise under a gentle stream of nitrogen 29.6 g (0.16 mol) of benzophenone imine (97% pure) dissolved in 25 ml of DMF, over the course of 2 h. The mixture was heated at about 100°C until ammonia evolution ceased. It was then cooled and 300 ml of ethanol were added. The product was initially oily and became solid after lengthy stirring. It was filtered off with suction and washed with ethanol.

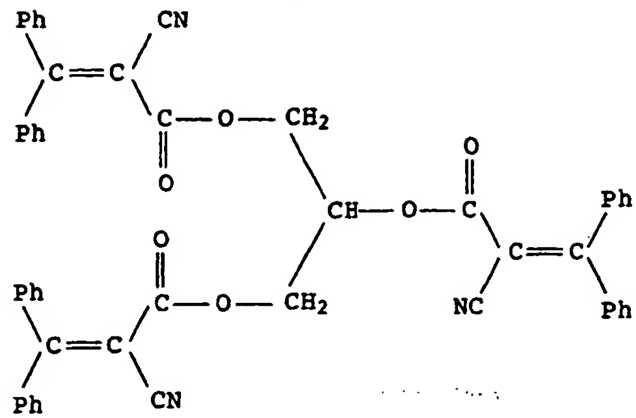
37.5 g (88.4%) of theory of the compound of the formula



were obtained with melting point 123–126°C (glassy); UV (CH_2Cl_2):λ_{max} = 310 nm, ε = 50,000.

Example 2

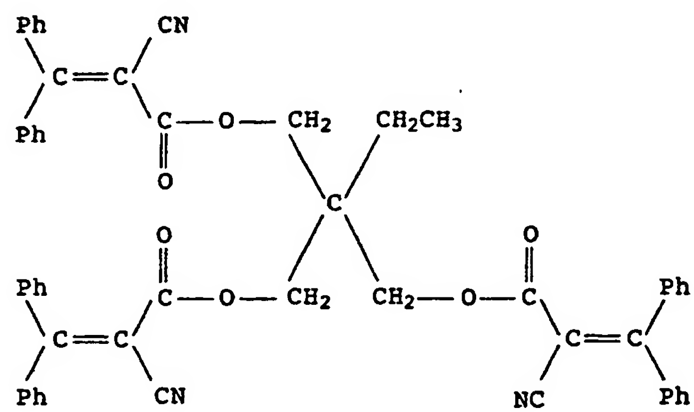
The compound of the formula



was prepared in a similar way to Example 1 from the appropriate cyanoacetic ester and benzophenone imine; melting point: 100–104°C; UV (CH_2Cl_2):λ_{max} = 310 nm, ε = 36,400.

Example 3

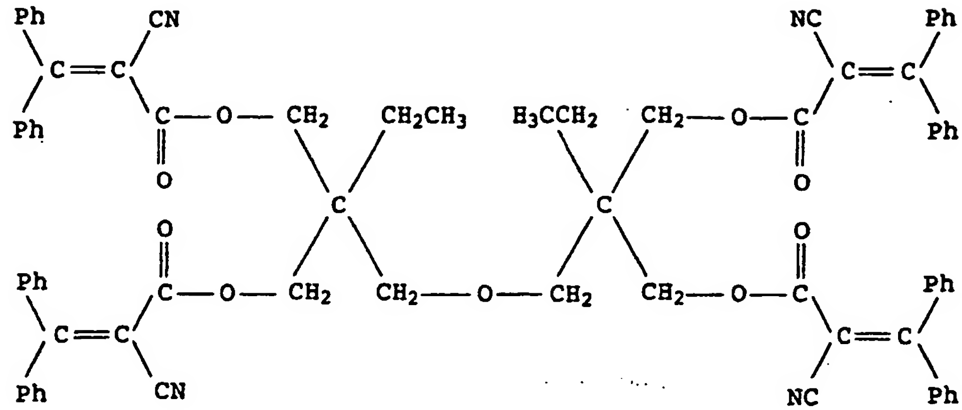
The compound of the formula



was prepared in a similar way to Example 1 from the appropriate cyano [sic] ester and benzophenone imine; melting point: 92°C; UV (CH_2Cl_2):λ_{max} = 308 nm, ε = 36,700.

Example 4

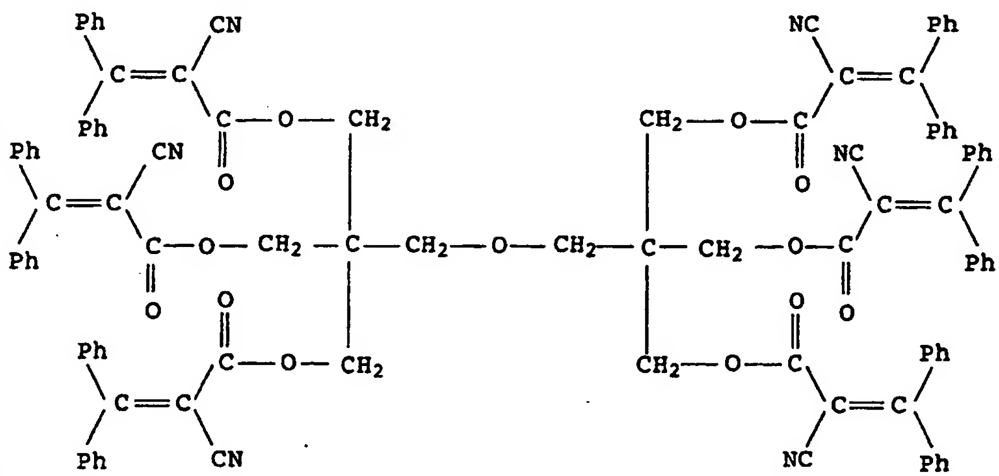
The compound of the formula



was prepared in a similar way to Example 1 from the appropriate cyanoacetic ester and benzophenone imine; melting point: 83–95°C; UV (CH_2Cl_2):λ_{max} = 308 nm, ε = 51,700.

Example 5

The compound of the formula



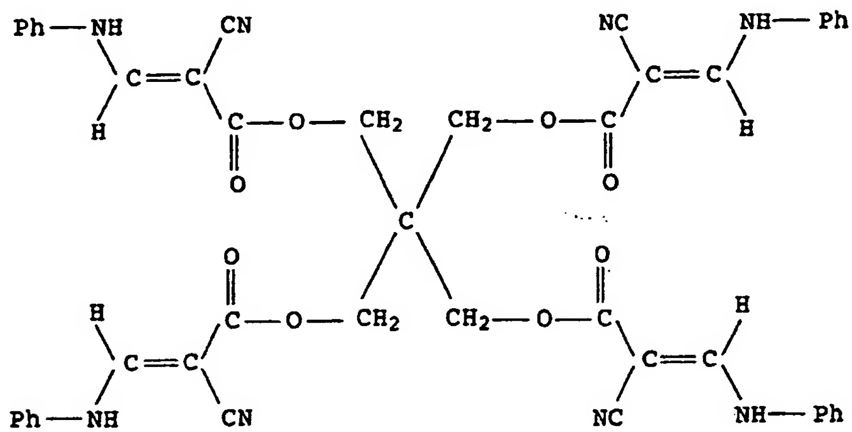
was prepared in a similar way to Example 1 from the appropriate cyanoacetic ester and benzophenone imine; melting point 124–128°C; UV (CH_2Cl_2):λ_{max} = 308 nm, ε = 76,000.

Example 6

30.3 g (0.075 mol) of 2,2-bis(hydroxymethyl)-1,3-propanediol tetracyanoacetate were refluxed with 29.8 g (0.32 mol) of aniline and 52 g (0.35 mol) of trimethyl orthoformate for 6 h. Then 80 ml of ethanol were added, and the suspension was refluxed for 1 h.

It was then filtered while hot under suction and the residue was thoroughly washed with ethanol.

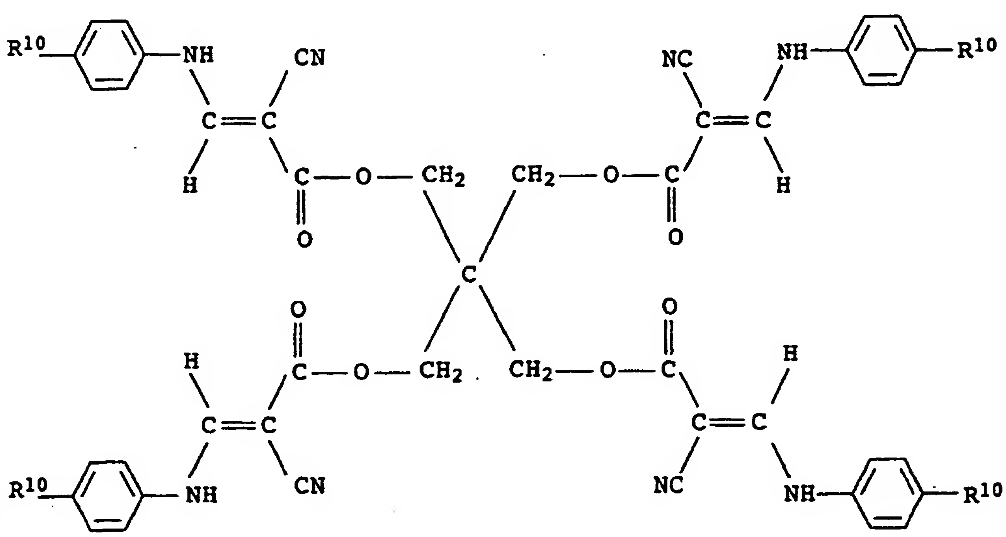
55 g (90% of theory) of a yellowish compound of the formula



were obtained with melting point 298–300°C; UV (DMSO): λ_{max} = 322 nm, ε = 98,000 (DMSO = dimethyl sulfoxide).

Examples 7 and 8

The compound of the formula



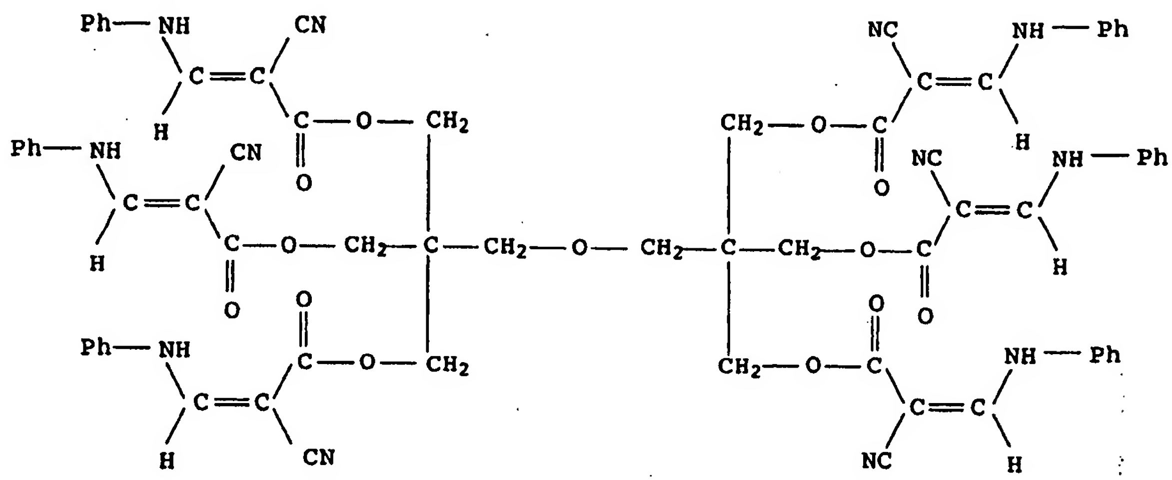
R^{10} = CH_3 (Example 7) or $COOCH_2CH_3$ (Example 8)

were [sic] prepared in a similar way to Example 6 from the appropriate cyanoacetic ester, the appropriate aromatic amine and trimethyl orthoformate; melting points: 321–323°C (Example 7) and

269–273°C (Example 8); UV (DMSO): λ_{max} = 326 nm (Example 7) and 334 nm (Example 8), ε = 99,000 (Example 7) and 150,000 (Example 8).

Example 9

The compound of the formula

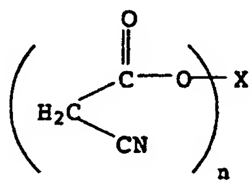


was prepared in a similar way to Example 6 from the appropriate cyanoacetic ester, aniline and trimethyl orthoformate; melting point 240-248°C; UV (CH_2Cl_2): λ_{max} =320 nm; ε = 145,000.

Examples 10-36

General preparation method for the reaction of cyanoacetic esters IV with aldehydes (R^1 or R^2 = hydrogen)

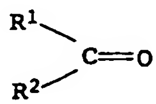
0.1 mol of an n-functional cyanoacetic ester IV,



IV

which has been obtained by reacting cyanoacetic acid with the appropriate n-hydric alcohol in a conventional way,

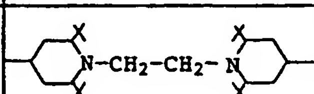
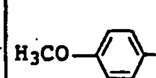
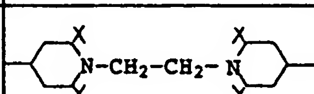
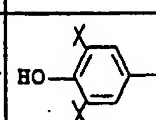
were [sic] reacted with 0.12 n mol of an aldehyde Vb

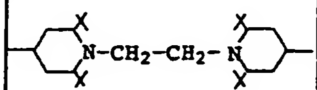
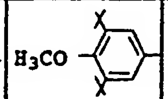
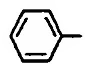
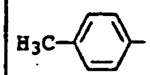
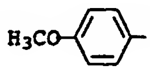
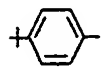
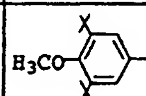
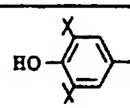
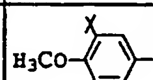
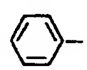
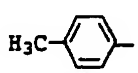
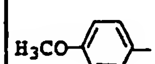
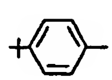


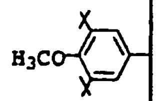
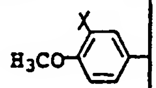
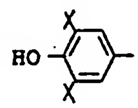
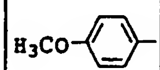
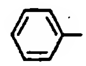
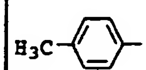
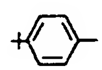
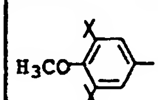
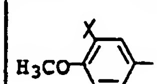
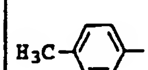
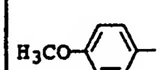
Vb

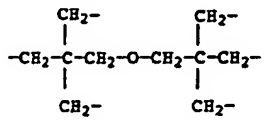
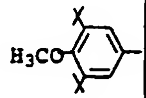
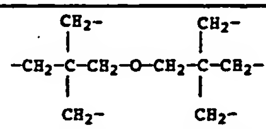
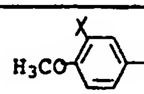
in 100 ml of N,N-dimethylacetammide [sic] in the presence of 0.5 ml of piperidine and 0.3 ml of glacial acetic acid. After 3 hours at 70°C, the precipitate was separated off, washed with methanol and water and dried.

Details of these experiments and the properties of the compounds I obtained are to be found in the following table.

No.	X	R^1 or R^2	* λ max [nm]	Molar extinction coefficient ε [$l \cdot cm^{-1} \cdot mol^{-1}$]	Melting point [°C]	Yield [%]
10			342	57 000	>265	95
11			350	59 000	>265	70

No.	X	R^1 or R^2	* λ max [nm]	Molar extinction coefficient ε [$l \cdot cm^{-1} \cdot mol^{-1}$]	Melting point [°C]	Yield [%]
12			336	47 000	>265	92
13	CH_2- $-CH_2-C-CH_3$ CH_2-		306	59 188	110-112	70
14	CH_2- $-CH_2-C-CH_3$ CH_2-		322	66 678	115-120	77
15	CH_2- $-CH_2-C-CH_3$ CH_2-		346	76 912	75-80	90
16	CH_2- $-CH_2-C-CH_3$ CH_2-		324	73 332	90-95	84
17	CH_2- $-CH_2-C-CH_3$ CH_2-		340	72 000	179-181	70
18	CH_2- $-CH_2-C-CH_3$ CH_2-		353	72 000	170-174	77
19	CH_2- $-CH_2-C-CH_3$ CH_2-		354	72 100	95-100	88
20	CH_2- $-CH_2-C-CH_2-CH_3$ CH_2-		306	58 256	114-116	63
21	CH_2- $-CH_2-C-CH_2-CH_3$ CH_2-		322	67 090	95-102	74
22	CH_2- $-CH_2-C-CH_2-CH_3$ CH_2-		346	75 519	30-35	73
23	CH_2- $-CH_2-C-CH_2-CH_3$ CH_2-		322	57 601	168-170	67

No.	X	R^1 or R^2	* λ max [nm]	Molar extinction coefficient ε [$l\cdot cm^{-1}\cdot mol^{-1}$]	Melting point [°C]	Yield [%]
24	$-CH_2-C(CH_2-)(CH_2-)-CH_2-CH_3$		338	68 000	103-105	74
25	$-CH_2-C(CH_2-)(CH_2-)-CH_2-CH_3$		354	72 000	85-87	74
26	$-CH_2-C(CH_2-)(CH_2-)-CH_2-$		358	106 480	275-276	66
27	$-CH_2-C(CH_2-)(CH_2-)-CH_2-$		346	102 298	215-216	90
28	$-CH_2-C(CH_2-)(CH_2-)-CH_2-$		308	63 909	148-155	79
29	$-CH_2-C(CH_2-)(CH_2-)-CH_2-$		324	102 273	250	79
30	$-CH_2-C(CH_2-)(CH_2-)-CH_2-$		324	101 131	130-131	67
31	$-CH_2-C(CH_2-)(CH_2-)-CH_2-$		342	51 000	98-100	60
32	$-CH_2-C(CH_2-)(CH_2-)-CH_2$		356	110 500	115-118	87
33	$-CH_2-C(CH_2-)(CH_2-)-CH_2-O-CH_2-C(CH_2-)(CH_2-)-CH_2-$		320	120 582	128-132	65
34	$-CH_2-C(CH_2-)(CH_2-)-CH_2-O-CH_2-C(CH_2-)(CH_2-)-CH_2-$		342	145 000	105-108	88

No.	X	R^1 or R^2	* λmax [nm]	Molar extinction coefficient ε [$l \cdot cm^{-1} \cdot mol^{-1}$]	Melting point [°C]	Yield [%]
35			338	149 300	150-151	58
36			352	145 000	135-140	51

* UV measurements in CH_2Cl_2

Example 37

Use Example: Migration test in polyethylene

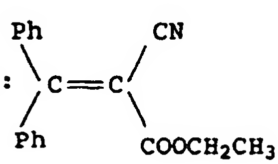
0.3% by weight of the UV stabilizer indicated below was dissolved in polyethylene by extrusion twice at a polymer temperature of 180°C, and then the polymer was granulated and blown to films 100 µm thick.

After storage at room temperature (20°C) or in an oven (50°C) for ten days, the surface of the film was assessed visually according to the following criteria:

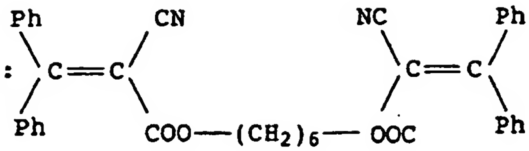
+	no deposit
o	slight deposit
-	heavy deposit

The following table shows the UV stabilizers used and the results of the tests:

UV stabilizer	Storage at 20°C	Storage at 50°C
Compound from Example No. 1	+	+
Compound A (for comparison)	o	-
Compound B (for comparison)	-	-

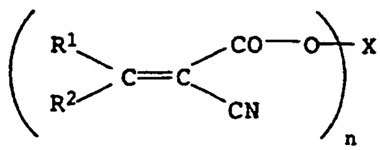
A: 

B (disclosed in(1)):



We claim:

1. A 2-cyanoacrylic ester of the formula I

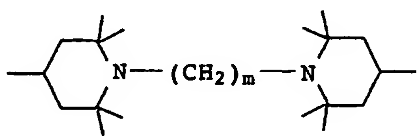


I

where R^1 and R^2 are each hydrogen or a radical having an iso- or heterocyclic ring system with at least one iso- or hetero-aromatic nucleus, and at least one of the radicals R^1 or R^2 must be different from hydrogen,

n is from 2 to 10, and

X is, when n = 2, a radical of the formula II

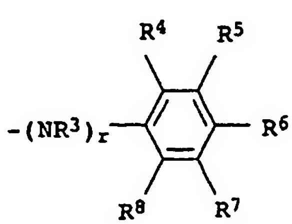


II

where m is from 2 to 8, and

X is, when n > 2, the radical of an n-hydric aliphatic or cycloaliphatic polyol having 3-20 carbon atoms, it also being possible for a cycloaliphatic radical to contain 1 or 2 hetero atoms, and for an aliphatic radical to be interrupted by up to 8 non-adjacent oxygen atoms, sulfur atoms, imino or C_1-C_4-alkylimino groups.

2. A 2-cyanoacrylic ester as claimed in claim 1, wherein one of the radicals R^1 and R^2 is a radical of the formula III



III

where R^3 is hydrogen or C_1-C_{10}-alkyl, r is 0 or 1, and R^4 to R^8 are each, independently of one another, hydrogen, C_1-C_8-alkyl, chlorine, bromine, cyano, nitro, amino, mono-(C_1-C_4-alkyl)amino, di(C_1-C_4-alkyl)amino, hydroxyl, C_1-C_8-acyl, C_1-C_8-acyloxy, C_1-C_{18}-alkoxy, C_1-C_{12}-alkoxycarbonyl, C_3-C_6-cycloalkyl or C_3-C_6-cycloalkoxycarbonyl.

3. A 2-cyanoacrylic ester as claimed in claim 1 or 2, wherein R^3 is hydrogen, methyl or ethyl.

4. A 2-cyanoacrylic ester as claimed in claims 1 and 2, wherein up to three of the radicals R^4 to R^8 are hydrogen, C_1-C_4-alkyl, chlorine, cyano, hydroxyl, acetyl, C_1-C_5-alkoxy, C_1-C_8-alkoxycarbonyl or cyclohexoxycarbonyl, and the remainder of these radicals are hydrogen.

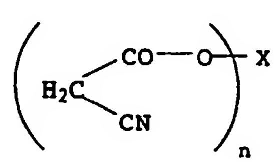
5. A 2-cyanoacrylic ester as claimed in claims 1 to 4, wherein R^6 is a hydroxyl group or a C_1-C_4-alkoxy group.

6. A 2-cyanoacrylic ester as claimed in claims 1 to 5, wherein R^5 and/or R^7 are hydrogen, methyl or tert-butyl.

7. A 2-cyanoacrylic ester as claimed in claims 1 to 6, wherein r is 0.

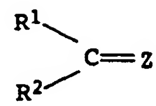
8. A 2-cyanoacrylic ester as claimed in claims 1 to 7, wherein X is the radical of an n-hydric polyol having 3 to 12 carbon atoms, which may be interrupted in its linear or branched carbon skeleton by up to 3 non-adjacent oxygen atoms, and n is from 3 to 6.

9. A process for preparing 2-cyanoacrylic esters as claimed in claims 1 to 8, where r is 0, which comprises reacting a cyanoacetic ester of the formula IV



IV

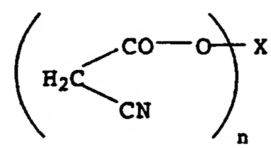
with n mol of a compound of the formula V



V

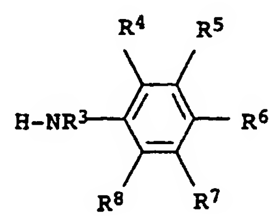
where Z is oxygen or NH, under the conditions of the Knoevenagel condensation in a polar solvent and in the presence of a catalyst.

10. A process for preparing 2-cyanoacrylic esters as claimed in claims 2 to 6 and 8, where r is 1, which comprises reacting a cyanoacetic ester of the formula IV



IV

with an aromatic amine of the formula Va



Va

in the presence of trialkyl orthoformate.

11. The use of the 2-cyanoacrylic esters as claimed in claims 1 to 8 as stabilizers, in particular against the action of light, for organic materials.

12. The use of the 2-cyanoacrylic esters as claimed in claims 1 to 8 as stabilizers, in particular against the action of light, in cosmetic or dermatological preparations.

13. The use of the 2-cyanoacrylic esters as claimed in claims 1 to 8 as stabilizers, in particular against the action of light, in plastics or paints.

14. Organic material stabilized against the action of light, oxygen and heat, which comprises from 0.01 to 10% by weight, based on the amount of organic material, of one or more 2-cyanoacrylic esters as claimed in claims 1 to 8.

15. A cosmetic or dermatological preparation stabilized against the action of light, oxygen and heat, which comprises from 0.01 to 15% by weight, based on the amount of this preparation, of one or more 2-cyanoacrylic esters as claimed in claims 1 to 8.

16. A plastic or paint stabilized against the action of light, oxygen and heat, which comprises from 0.01 to 10% by weight, based on the amount of the plastic or paint, of one or more 2-cyanoacrylic esters as claimed in claims 1 to 8.